

Singlet Vinylcarbenes: Spectroscopy and Photochemistry

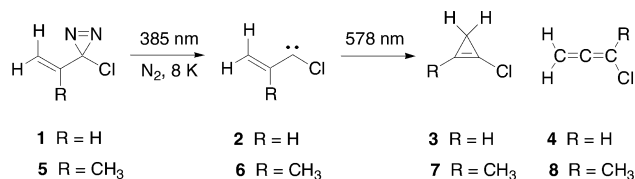
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In contrast to arylcarbenes, there is scant spectroscopic information available on their simpler delocalized cousins, vinylcarbenes. Thus, although extensive experimental data exist for both singlet¹ and triplet arylcarbenes,² direct characterization of vinylcarbenes has been limited to a select few triplet species by EPR³ and IR spectra.⁴ Spectroscopic information on singlet vinyl carbenes is nonexistent. Ironically, vinylcarbenes, particularly in their singlet states, play a central role in thermal and photochemical cyclopropene isomerizations,⁵ as well as in a wide variety of useful synthetic applications.⁶ We are pleased to report the first spectroscopic characterization of several singlet vinylcarbenes, together with an investigation of their photochemical transformations. Moreover, we describe the cyclization of one of these species to a highly strained bicyclo[3.1.0]hexene.

Halogen substitution is well-known to stabilize carbene singlet states, enabling the spectroscopic investigation of even highly reactive species.⁷ Although halodiazirines are the most convenient precursors to a broad range of halocarbenes,⁸ we were concerned that the usual Graham⁹ oxidative cyclization conditions might prove too harsh for vinyl substituted systems. However, in his seminal paper, Graham alluded to the generation of vinylchlorodiazirine **1** but reported no details of its chemistry.⁹ We found that the usual hypochlorite oxidation of the corresponding amidine indeed produced **1** in acceptable yield as an unstable oil, which we characterized by NMR, UV/vis, and IR spectroscopy.¹⁰ Irradiation of N₂ matrix isolated **1** at 8 K (385 nm, 1.5 h) gave vinylcarbene **2**, as supported by comparison of its spectra to calculation (vide infra) as well as by its subsequent photochemistry.^{11,12} The carbene exhibited its strongest bands in the IR at 1573, 1389, 1158, and 965 cm⁻¹, together with a broad absorption in the UV/vis spanning 550–850 nm (λ_{max} 690 nm). The carbene was stable for several days in N₂ at 9–25 K in the dark, but subsequent irradiation of the matrix at 578 nm rapidly converted **2** to a mixture of cyclopropene **3** and allene **4**, confirmed by IR spectroscopy (Figure 1).¹³



B3LYP/6-31+G** calculations locate two energy minima for **2**, a planar *s-E* conformer shown, and an *s-cisoid* conformer twisted somewhat (42° out of plane) due possibly to steric interactions (and predicted to lie 4.2 kcal/mol higher in energy). The IR spectra similarly display two sets of bands for **2** (Figure 1). One set of absorptions, which fits the predicted IR spectrum for the *s-cisoid* conformation, is particularly photolabile, converting to products after only brief irradiation at 578 nm. The other set, consistent with predicted spectra for *s-E* **2**, disappears more slowly at this wavelength. Comparison to calculated IR band intensities suggests that, at most, 10% of the *s-cisoid* conformer is produced from **1**.

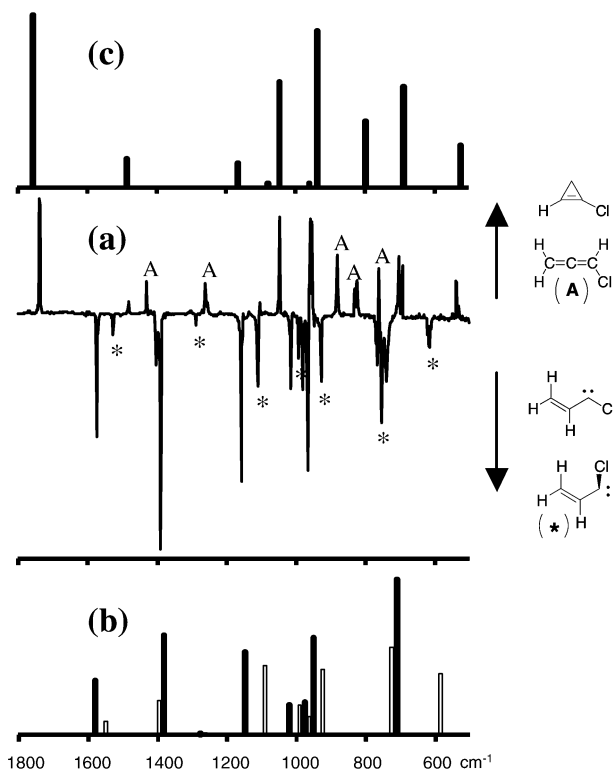
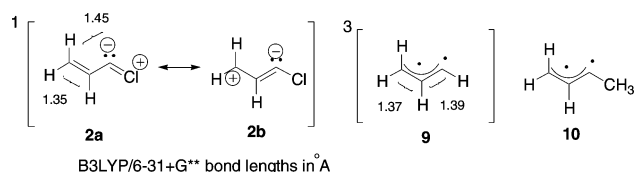


Figure 1. (a) IR difference spectra (arbitrary absorbance units) showing bleaching of carbene **2** (“down bands”) on 1 h irradiation at 578 nm (products **3** and **4** “up bands”). Bands labeled * assigned to more labile *s-cisoid* conformer of **2** (see text), and those labeled A assigned to allene **4**. (b) B3LYP/6-31+G** calculated IR spectrum for carbene **2**; *s-E* filled bars, *s-cisoid* open bars; (c) B3LYP/6-31+G** calculated IR spectrum for cyclopropene **3**. All calculated frequencies are scaled by 0.97 factor.¹²

Propenyldiazirine **5** could be produced similarly by Graham oxidation of the corresponding amidine.¹⁰ Irradiation of **5** at 8 K in a N₂ matrix (385 nm, 40 m) gave chlorocarbene **6**, with strongest IR bands at 1311 and 844 cm⁻¹ and a broad UV/vis absorption centered at 680 nm. The IR and visible spectra fit those predicted for **6** at the B3LYP/6-31+G** level. Irradiation of matrix isolated **6** at 578 nm produced mainly methylchlorocyclopropene **7**, by comparison to DFT calculated IR spectra, but small amounts of methyl-shifted allenic product **8** cannot be ruled out (Figure S-2, Supporting Information).¹⁰

It is interesting to note the significant structural differences that are calculated between the chlorovinylcarbene **2** and the parent vinylcarbene **9**, which directly lead to major spectroscopic consequences. Calculations indicate that vinylcarbene **9** is a ground-state triplet carbene, with a predicted triplet–singlet (S–T) energy gap of ca. 12 kcal/mol.^{14,15} The carbene is predicted to have the highly delocalized allylic diradical structure shown below.⁴ Although both *s-E* and *s-Z* planar conformations are found to be energy minima for the triplet carbene, only *s-E* is shown. As with other halocar-

benes, vinylchlorocarbene **2** is predicted to be a ground-state singlet. At the B3LYP/6-31+G** level, the triplet state of carbene **2** lies 1.3 kcal/mol higher (*s-E*, vibrationally corrected). For reference, at this level of theory, the S–T gap in phenylchlorocarbene is calculated to be 4.6 kcal/mol, a bit lower than estimates at higher levels (7.8 kcal/mol at the QCISD(T) level).¹ In contrast to vinylcarbene/triplet diradical **9**, the calculated geometry for singlet carbene **2** reflects only minor delocalization with typical short C=C and long C–C bonds. Natural resonance theory (NRT)¹⁶ calculations based on the B3LYP electron densities indicate that resonance structures **2a** and **2b** contribute ca. 82 and 12%, respectively, to the electronic structure of **2**.

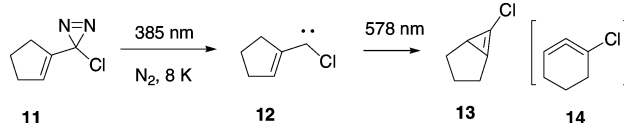


Maier and co-workers⁴ have reported recently that UV irradiation of 1-methylcyclopropene in Br₂-doped Xe matrices at 10 K produced triplet methylvinylcarbene **10**, which could be characterized by IR spectroscopy. Similar photolysis of cyclopropene itself was suggested to give a trace of the parent triplet vinylcarbene (**9**). The reported IR spectra for triplet **10** are consistent with a delocalized allylic structure, with the absence of a C=C stretching absorption in particular. In contrast, chlorocarbene **2** displays a strong C=C stretch at 1573 cm⁻¹ (compared to 1587 cm⁻¹ calculated for *s-E*, scaled by 0.97),¹² consistent with its localized structure. As expected, calculated IR spectra for both conformers of triplet **2** are inconsistent with experiment.¹² TD-DFT calculations for **2** and **6** (743 nm for *s-E* **2** and 761 nm for *s-E* **6**) are likewise consistent with the experimental visible absorptions, showing $\sigma-\pi^*$ transitions typical for singlet carbenes (cf. 700–750 nm for phenylchlorocarbene¹).

A transition state was located for the cyclization of *s-E* **2** to **3** at the B3LYP level. The activation barrier for this process, vibrationally corrected, is predicted to be 12.3 kcal/mol. Although rearrangement to give chloroallene (**4**) is calculated to be thermodynamically more favorable (ca. exothermic by –40 vs –17 kcal/mol), the carbenic p-orbital is improperly aligned for the H-shift, and the energy barrier is predicted to be 19.7 kcal/mol.

The synthetic methodology employed in this study appears to be quite general, and we have found that cyclic singlet chlorovinylcarbenes can also be generated and characterized in similar fashion. For example, 385 nm irradiation of the cyclopentenyl-diazirine **11** matrix isolated in N₂ at 8 K produced the corresponding carbene **12**, signified by strong IR bands at 1549 and 741 cm⁻¹, together with a broad visible absorbance centered at 658 nm. Calculated IR and Uv/vis spectra for the *s-Z* and *s-E* conformations of the carbene are very similar, and although they fit the experimental spectra closely, they do not allow us to distinguish whether one or more conformations are in our experiments. Irradiation of **12** at 600 nm rapidly converts the carbene to a new product with a strong IR band at 1751 cm⁻¹. The calculated IR spectra are most consistent with formation of the highly strained¹⁷ bicyclopropene **13** as the major product, although it is impossible to rule out the presence of the ring-expanded allene, **14** (Figure

S-3, Supporting Information). Interestingly, calculations indicate that formation of **13** from **12** is only ca. 1 kcal/mol exothermic.



In sum, we have shown for the first time that a variety of chlorovinylcarbenes can be generated from the corresponding diazirines. This synthetic route makes these singlet vinylcarbenes accessible for spectroscopic interrogation and promises broader application.¹⁸

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Supporting Information Available: Synthetic, spectroscopic, and calculational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Synthetic and other experimental details are described in the Supporting Information.
- (11) For a general description of the matrix isolation instrumentation, see: Rempala, P.; Sheridan, R. S. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2257 and references therein.
- (12) Details of the calculations, and theoretically predicted spectra, are given in the Supporting Information.
- (13) Identification of **3** and **7** was by comparison to calculated IR spectra,¹² and **4** was characterized both by comparison to the spectra of authentic material and by calculation. Surprisingly, **4** shows only a weak allenic stretch. On the basis of theoretical IR band intensities, we estimate a ca. 2:1 ratio of **3**:**4** is produced. Alkyne products from potential alternate H-shifts were not observed. Minor amounts of a second conformer were similarly observed in matrix spectra of **6**.
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